

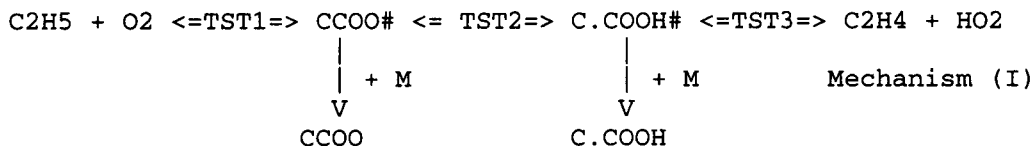
Pathway and Kinetic Analysis on the Propyl Radical + O₂ Reaction System

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Abstract:

The reaction of alkyl radicals with molecular oxygen plays a key role in the oxidation of alkanes. In the negative temperature coefficient region of alkane oxidation, this reaction leads to the production of alkenes, oxygenates and chain branching. At higher temperatures, it leads primarily to the production of a conjugate alkene and the HO₂ radical. The reaction of alkyl radicals with O₂ is important in atmospheric chemistry and in many practical combustion problems including automotive and gas turbine engines. In the case of C₂H₅ + O₂, it was generally accepted that the reaction proceeds to C₂H₄ through the path:



Recent work by Schaefer and coworkers using density function theory has suggested a fourth transition state (TST4), where direct production of ethylene + HO₂ can result from concerted elimination of HO₂ from CCOO#. This postulated reaction path does not proceed through the hydroperoxy - ethyl radical (C.COOH) intermediate. The existence of the cyclic transition state was first hypothesized by McAdam and Walker. They reported that Mechanism (I) could not explain the observed pressure dependence of C₂H₅ + O₂ = C₂H₄ + HO₂ at 298 K and the observed decrease in rate constant with increasing temperature from 653-773 K. They suggested the existence of a long-lived, cyclic transition state and a concerted elimination of ethylene would explain these experimental observations. In subsequent work, Gutlati and Walker postulated the existence of an analogous, long-lived, cyclic transition state for the i-C₃H₇ + O₂ system as well. Wagner, Bozzelli and Dean, and Kaiser have, however, shown that Mechanism I can explain the observed temperature and pressure dependencies. The propyl + O₂ system that is addressed in the present work.

In this study, we analyze the propyl + O₂ reaction system using thermochemical kinetics, Transition State Theory (TST), molecular thermodynamic properties, quantum Kassel analysis (quantum RRK) for k(E) and modified strong collision analysis for fall off. Cyclic transition states for both hydrogen transfer and concerted elimination of propylene are calculated using semi empirical (Mopac PM3) theory in addition to transition states for the CCC. + O₂ addition and HO₂ elimination. Computed rate constants are used in a detailed chemical kinetic mechanism and compared to the n-propyl + O₂ data of Slagle et al. (1984). They measured the rate of disappearance of n-propyl by reaction with O₂ over a temperature range of 297 to 635 K and a pressure range of 0.4 to 7 Torr, as well as the fall off data of the Kaiser research group.

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